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SYNTHESIS OF LEAD PORPHYRIN DERIVATIVES BY A SOLID STATE REACTION

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ABSTRACT

A solid state reaction was successfully applied for the first time to synthesize complexes of lead(II) with the porphyrin derivatives *meso*tetra(4-hydroxyphenyi)porphyrin, *meso*-tetra(4 methoxyphenyl)porphyrin and *meso*-tetra(4-nitrophenyl)porphyrin. The influence of the composition and structure of the porphyrin, temperature, initiator and mixing degree on the reactions was studied. IR,UV absorption and fluorescence spectra show the compositions and structures of the complexes are the same as those synthesized in solution.

INTRODUCTION

The structures and properties of porphyrins and metalloporphyrins have been studied in great detail. They may be used as catalysts¹, anticancer and photodynamic therapy $drugs^{2,3}$, photosensitive agents^{4,5}, and so on. Thus,

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it is very important to synthesize porphyrin complexes. To date, metallo porphyrin complexes have been prepared by refluxing the reactants in a solvent and, the separation and purification of the products was sometimes very difficult.

Recently, solid state reactions have been used to synthesize complexes and solid materials, for example, metal complexes of bipyridine and phenanthroline⁵. In this paper, solid state reactions were applied for the first time to synthesize the lead(II) porphyrin derivatives of *meso*-tetra(4 hydroxyphenyl) porphyrin (H₂THPP), *meso*-tetra(4 methoxyphenyl) - porphyrin (H₂TMOPP) and *meso* tetra(4 mitrophenyl)porphyrin (H₂TMOPP) (Fig. 1). The experimental results show that a new synthesis method for metallo porphyrin complexes has been developed. This method of synthesis is general, convenient and free from side reactions, gives high yields and requires no special reagents.

EXPERIMENTAL

Preparation of Complexes by the Solid State Reaction

Lead(II) acetate monohydrate (0.0686 g, 0.2 mmol) and $\rm H_2THPP(0.1356$ g, 0.2 mmol) (1 : 1 molar ratio) were mixed, one drop of acetone was added and the mixture ground in an agate mortar for 20 minutes. The progress of the reaction was monitored by UV absorption spectra at 350–700 nm in DMF solution. The product may be purified by column chromatography on $\rm Al_2O_3$ with CHCl₃ 30 mL as eluate on a 20 cm \times 3 cm diameter column. The product was allowed to crystallize by slow evaporation of the solvent. The yield was 0.162 g (92 %). The other complexes were synthesized by a similar procedure.

Preparation of the Lead(II) Porphyrin Complexes in Solution

The metal porphyrin complexes were also prepared as described in the literature⁷ by refluxing lead(II) acetate monohydrate (0.171 g, 0.5 mmol) and



Fig. 1. Structure of the Porphyrins

the porphyrin (0.5 mmol) in 40 mL DMF for 70 minutes. The volume of the solution was decreased and then the solution was cooled in an ice water bath. CH_3OH $CHCl_3(2:1 v/v)$ 20 mL was added and the resulting partially crystalline precipitate was filtered and washed with CH_3OH until the filtrate was clear. The products were purified by chromatography on an alumina column and recrystallization from CH_3OH - $CHCl_3(5:1 v/v)$ 30 mL. The elemental analyses results were the same as those synthesized in the solid state.

RESULTS AND DISCUSSION

Effect of Experimental Conditions

The green lead complexes form in the solid state by the following reaction:

 H_2P + $Pb(CH_3COO)_2 \rightarrow PbP$ + 2 CH_3COOH

where H_2P is the porphyrin. Although this reaction is the same as it occurs in solution, but the rate is faster, and the yield is high.

The reaction rate and conversion are related to various factors including reactant structure, reaction temperature, mixing degree and initiator. For temperature, the reaction was completed in over 2.0 h at room temperature the yields were as follows: 0.13 g (74.4%) for PbTHPP; 0.11 g (60.1%) for PbTMOPP and 0.10 g (50%) for PbTNPP and in 1.5 h at 35°C, the yields were: 0.15 g (90.8%) for PbTHPP, 0.16 g (82.2%) for PbTMOPP and 0.16 g (80.3%) PbTNPP. In the presence of a small amount of acetone, the reactions are completed in 30 min at 35°C; the yields were 91.2% for PbTHPP, 85.2% for PbTMOPP and 83.9% PbTNPP, thus it appears the reaction is catalyzed by acetone. It may be that the liquid acetone can transfer and exchange matter and energy between the reactants.

The reactant structure also influences the reaction rate. Experiments show that the rates for different porphyrins are different. The reaction of lead(II) acetate with H_2 THPP is the fastest, and that with H_2 TMOPP is the slowest.

The mixing degree may be correlated with the grinding time. It is necessary for all reactions to grind the reactants for 10 min in order to obtain a higher rate and yield. The results of elemental analyses and yields are shown Table I and compared with the results of compound, which were synthesized in solution. The properties of the products are the same as that of compound synthesized in solution, such as IR and UV spectra.

Visible Absorption Spectra

The absorption spectra shown in Figs. 2-4 were measured on a UV-240 model spectrophotometer(Shimadzu, Japan). The spectra measurements in DMF as solvent in the range of 350 700 nm were carried out for the porphyrin and the complexes. Figs. 2-4 show a very intense absorption peak at 350-500 nm (Soret band) for the porphyrins and their complexes. There are various absorption peaks for the ligands and the complexes in the range of 500-700 nm with much less intensity (Q band). The extinction coefficients and absorption wave lengths are shown in Table II.

Fluorescence Spectra

The flucrescence spectra were determined on a 850 model fluorescence spectrophotometer(Shimadzu, Japan). Every porphyrin ligand has a very

Table I. Analysis Results of Lead Porphyrin Derivatives

Compound	Formula	Yield	M. P.	Calcu	lated	(%)		Found	
	"ergnes	(75)		C	Н	N N	(`	H	<u>N</u>
Р6С ₄₄ Н ₂₈ N ₄ 0 ₄ (Р6НТРР)	883	92 (78)	278 (278)	59.80	3.17	6. 34	59.77 (59.75)	3.20 (3.22)	6, 34 (6, 30)
PbC ₄₈ H ₃₆ N ₄ 0 ₄ (PbTMOPP)	943	88 (82)	254 (254)	61.34	3.83	5.96	61.33 (61.35)	3, 85 (3, 85)	5.95 (5.94)
PbC ₄₄ H ₂₈ N ₈ O ₈ (PbTNPP)	1003	86 (75)	285.5 (285.5)	52.64	2. 79	11.17	52.64 (52.62)	2 80 (2,82)	11.16 (11.15)

The data in parentheses are the results of products synthesized in solution.



Fig.2.Absorption Spectra of H₂THPP and its Complex: Solid Line, H₂THPP; Dashed Line, Complex



Fig.3. Absorption Spectra of H_2 TMOPP and its Complex: Solid Line, H_2 TMOPP; Dashed Line, Complex

Fig.4. Absorption Spectra of H₂TNPP and its Complex: Solid Line, H₂TNPP; Dashed Line, Complex

intense fluorescence emission peak in ethanol solution in the range of 600-800 nm, but the complexes have no fluorescence at all. These results are the same in various other solvents such as DMF, dioxane or acctone. The evidence of complex formation is the disappoarance of the fluorescence of the porphyrin derivatives.

Infrared Spectra

The infrared spectra were determined on a Fourier-Transform infrared spectrometer (Bruker, Vector 22). The main absorption bands of porphyrin and metalloporphyrin derivatives in the range of 4000-400 cm⁻¹, as well as the intensities and assignments to various modes of vibration according to the literature^{8,9}, are listed in Table III.

The weak N-H stretching vibration above 3318 cm⁻¹ for the ligands disappears in the complexes, since the acidic N-H hydrogen atoms are replaced by lead(II). The disappearance of the weak N H absorption band is

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Sample	Soret band (ɛ'x	(10^4) Q band (ϵ ' x 10 ⁴)
H ₂ THPP	422 (46)	519 (3.8), 557 (3.4), 596 (1.3), 653 (1.7)
PbTHPP	469 (44)	361 (12.3), 434 (18.8), 447 (7.2),
		561 (1.2), 616 (2.1), 667 (2.3)
	•469(44)	261 (12.3), 434 (18.8), 447 (7.2),
		561 (1.2), 616 (2.1), 667 (2.3)
H ₂ TMOPP	421 (49)	517 (4.2), 552 (3.2), 592 (1.4), 650 (2.1)
PbTMOPP	470 (50)	361 (12.0), 434 (15.3), 447 (7.3),
		586 (1.9), 617 (2.2), 668 (3.3)
	•470 (50)	361 (12.0), 434 (15.3), 447 (7.3),
		586 (1.9), 617 (2.2), 668 (3.3)
H ₂ TNPP	422 (48)	514 (3.9), 529 (2.2), 587 (1.9), 643 (1.4)
PbTNPP	473 (45)	361 (12.1), 434 (12.8), 447 (7.1),
		528 (1.4), 596 (1.8), 660 (2.1)
	•473(45)	361 (12.1), 434 (12.8), 447(7.1),
		528 (1.4), 596 (1.8), 660 (2.1)

Table II. UV Spectral Data of Porphyrins and Lead Porphyrins (in DMF)

The data are the results of products synthesized in solution.

also evidence of complex formation. The replacement of the imino hydrogen atoms results in shifts of many absorption bands of the ligands to higher or lower frequencies. The suggested structure of the lead porphyrin complexes is shown in Fig. 5.

CONCLUSION

Solid state reaction conditions were applied to synthesize lead(II) porphyrin derivatives in high yields. The method is simple, convenient and suitable for the synthesis of metalloporphyrin complexes. The composition and structure of the reactants, reaction temperature, initiator and degree of mixing affect the rate and degree of the solid state reactions. Higher

H ₂ THPP	PbTHPP	H ₂ TMOPP	Pbtmopp	H_2 TNPP	PbTNPP	Assignment.
3482 m	3495 m					v (0-11)
(3482 m)	(3495 m)					
3318 w		3321 w		3321 m		v (N-H)(pyrrole)
(3318 w)		(3321 w)		(3321 m)		
3104 w	3112 w	3104 w	3109 m	3104 w	3112 w	
(3104 w)	(3112 w)	(3104 w)	(3109 m)	(3104 w) (3112 w)	
3073 w	3075 w	3073 w	3075 w	3073 w	3073 w	
(3073 w)	(3075 w)	(3073 w)	(3075 w)	(3073 w) (3073 w)	
2930 m	3071 m	2931 m	2925 m	2930 m	2928 m	v (C_H)
(2930 m)	(3071 m)	(2931 m)	(2925 m)	(2930 m) (2928 m)	
2853 w	2854 w	2853 w	2853 w	2853 w	2853 w	
(2853 w)	(2854 w)	(2853 w)	(2853 w)	(2853 w) (2853 w)	
2355 w	2359 w	2355 w	2359 w	2355 w	2359 w	
(2355 w)	(2359 w)	(2355 w)	(2359 w)	(2355 w) (2359 w)	
2326 w	2330 w	2325 w	2325 w	2325 w	2325 w	
(2326 w)	(2330 w)	(2325 w)	(2325 w)	(2325 w) (2325 w)	
1602 s	1607 m	1609 s	1608 s	1595 s	1596 s	v (C-C)(benzal)
(1602 s)	(1607 m)	(1609 s)	(1608 s)	(1595 s) (1596 s)	
1580 m	1591 m	1575 m	1579 m	1575 m	1575 w	v (C-C)
(1580 m)	(1591 m)	(1575 m)	(1579 m)	(1575 m) (1575 w)	(Conj. Phenyl)
				1518 s 1	515 s	v (NO ₂)
				(1518 s) (1515 s)	
1510 s	1508 s	1510 s	1504 s	1510 s	1504 s	v (C-C) (benzal)
(1510 s)	(1508 s)	(1510 s)	(1504 s)	(1510 s) (1504 s)	
1475 m		1475 m		1475 m		v (C-N)
(1475 m)		(1475 m)		(1475 m)		
1460 m	1448 m	1461 m	1440 m	1456 m	1439 m	
(1460 m)	(1448 m)	(1461 m)	(1440 m)	(1456 m) (1439 m)	
1462 m	1455 s	1467 m	1467 m	1458 m	1456 m	$\delta_{as}(N-H)$ (pyrrole)
(1462 m)	(1455 s)	(1467 m)	(1467 m)	(1458 m) (1456 m)	
1350 s	1346 s	1347 s	1345 s	1347 s	1345 s	δ (=C-H)
(1350 s)	(1346 s)	(1347 s)	(1345 s)	(1347 s) (1	345 s)	
		1247 s	1247 s			v (C-0)
		(1247 s)	(1247 s)			
1213 s	1206 m	1214 s	1208 m	1211 s	1208 s	v (C-C)
(1213 s)	(1206 m)	(1214 s)	(1208 m)	(1211 s) (1208 s)	
1171 s	1168 ш	1171 s	1177 s	1175 m	1177 m	

Table III. IR Data of Porphyrins and Lead Porphyrins

Table III. Continued

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(1171 s)	(1168 m)	(1171 s)	(1177 s)	(1175 m)	(1177 m)	
1107 s	1110 s	1106 s	1108 s	1107 s	1110 m	v (C=C)
(1107 s)	(1110 s)	(1106 s)	(1108 s)	(1107 s)	(1110 m)	(<i>p</i> -Subst.phenyl)
991 m	1002 m	993 m	1002 m	1008 m	1013 m	v (C-H)(pyrrole)
(991 m)	(1002 m)	(993 m)	(1002 m)	(1008 m)	(1013 m)	
9 6 8 m		968 m		968 m		δ (N-H)(pyrrole)
(968 m)		(968 m)		(968 m)		
847 m	846 m	847 m	847 m	847 m	847 m	v (C-N) (pyrrole)
(847 m)	(846 m)	(847 m)	(847 m)	(847 m)	(847 m)	
799s	800 s	801 s	803 s	800 m	803 s	v (C-H)
(799s)	(800 s)	(801 s)	(80 3 s)	(800 m)	(803 s)	(p-disubst.phenyl)

The data in parentheses are the results of products synthesized in solution.



Fig. 5. Suggested structure of the Complexes

temperature, presence of initiators and higher mixing degree result in an increase of the reaction rate. The reaction rates of various ligands are different, the rate order is: $H_2THPP > H_2TMOPP$. IR, UV and fluorescence spectra and elemental analyses show that composition and structure of the complexes are the same as those synthesized in solution.

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